PHYSICAL BENEFICIATION OF CHAR AND CHEMICALLY CONDITIONED COAL

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ABSTRACT

Demineralization of coals and coal-derived chars is part of an effort to develop alternative fuels from coal. Pyrolysis and some gasification processes yield chars containing a large fraction of the calorific value of the feed coal and essentially all of its mineral matter. In the work reported here, three gasification chars produced from anthracite, bituminous, and subbituminous coals have been subjected to specific gravity separation to determine their yield-ash relationships. Either low yields or high ash levels in the float products were observed. Also reported is preliminary work concerning the use of chemical conditioning to enhance the cleanability of coal prior to physical beneficiation. Conditioning of an Illinois No. 6 River King Mine coal with either supercritical methanol or cyclohexane resulted in an improved yield-ash relationship, whereas similar treatment with supercritical toluene had a negative effect.

INTRODUCTION

Currently, there is increasing interest in the identification, development, and characterization of new coal-derived fuels which have application extending beyond traditional electric utility markets into the commercial, industrial, residential, and transportation sectors of our economy. To penetrate these markets, new fuels must be low in both total sulfur and mineral matter. Emphasis is therefore being placed on the development of new processes to provide ultraclean coal having less than one percent mineral matter. In one recent example coal is subjected to physical beneficiation, pyrolysis, and subsequent beneficiation of the char [1]. In this scheme, a portion of the char is combined with the pyrolysis liquids to produce a heavy oil substitute. In order for the process to be profitable, however, the excess char must be sold at a premium price, such as in the residential heating market.

Results from two different areas of research concerned with the development of alternative fuels from coal will be presented in this paper. The first area involves beneficiation of chars produced from coal. Such chars may be a major product of gasification and pyrolysis processes used to produce premium liquid and gaseous fuels. Since a large portion of the calorific value often ends up in the char, the beneficiation of this material to produce a premium fuel can be important from a process economics standpoint.

The second area of research is concerned with the use of a chemical pretreatment to improve mineral matter liberation during subsequent physical beneficiation. Advantages of this reversal of the conventional order of treatment have been discussed elsewhere [2]. Reported here are preliminary results from the use of supercritical fluids in the initial chemical-pretreatment step.

For reasons of clarity, the following discussion of methodology and results is divided into two parts. The first section describes the beneficiation of the gasification chars, and the second the work on conditioning of coal prior to its physical beneficiation. After this, an overall conclusion section summarizes both areas of research.

I. BENEFICIATION OF GASIFICATION CHARS

EXPERIMENTAL

Three gasification chars produced at the Pittsburgh Energy Technology Center were used for the beneficiation tests. These chars were formed from three different coals: a Pennsylvania anthracite coal, a Pittsburgh seam bituminous coal from the Bruceton Experimental Research Mine, and a Montana subbituminous coal from the Rosebud Mine. These coals were gasified at approximately 1160 K under a combined oxygen/steam pressure of 4.1 MPa in the Synthane Process Development Unit (PDU) gasification system. The PDU system combined the steps of fluidized-bed pretreatment, free-fall carbonization, and fluidized-bed gasification [3]. Table 1 contains the analysis of the three chars used.

Beneficiation of the gasification chars involved a washability determination on the char as received and after additional crushing. A high-speed centrifuge equipped with four 0.5 L hourglass-shaped flasks was used to effect the specific gravity separations. Enough heavy organic liquid was added to fill each centrifuge flask just above the neck. The specific gravity was checked with a spindle hydrometer to within ± 0.001 of a specific gravity unit.

Four 25-gram samples were riffled from each char using a microsplitter. The 25-gram char samples were then added to the flasks along with enough additional liquid to bring the liquid level to within 1.5 cm of the top of the flask. The samples were centrifuged for 20 minutes at 1500 rpm, and the centrifuge was allowed to stop without braking. After removing the flasks, thin rubber inserts were put in the necks, and the float products were carefully poured off. The rubber inserts were removed to recover the sink products. Both products were vacuum filtered to remove the heavy liquid, air dried, and weighed.

The total sink product was divided into two or four equal portions by weight and then added to the centrifuge flasks containing the next higher specific gravity liquid. This procedure was repeated for each specific gravity. Each product was analyzed for calorific value, ash, and total sulfur. All results are tabulated as cumulative values and are reported on a moisture-free basis.

Another riffled portion of each char sample was crushed to either 200- or 325-mesh top size, and similar tests and analyses were performed to determine the effects of crushing on the liberation of ash and its subsequent removal.

DISCUSSION OF RESULTS

The results of the specific gravity separations for the three as-received and crushed chars are contained in Tables 2, 3, and 4. For the anthracite coal gasification char shown in Table 2, the as-received sample contained 69.7 wt% plus-200-mesh material. After crushing, 91.9 wt% of the sample was minus-325 mesh. For the as-received sample, 79.1 wt% could be recovered at 2.00 specific gravity, analyzing 7.6 wt% ash. This represents a 54% ash reduction. After crushing, only 44.0 wt% was recovered at the same specific gravity, and only a 10% ash reduction was observed.

The data for the bituminous coal gasification char are contained in Table 3. Initially 76.5 wt% of the char was plus-200 mesh. After crushing, all of the sample was minus-200 mesh. At a specific gravity of 1.80, 87 wt% of the char was recovered; however the ash reduction was only 28%. After crushing, the ash content of the float 1.80 specific gravity product was only 4.1 wt%, but the weight recovery was only 20.5%.

Table 4 contains the results for the subbituminous coal gasification char. The as-received char contained 44.7 wt% plus-200-mesh material. After crushing, 96.8 wt% was minus-200 mesh. The float-sink tests show a 72% ash reduction for the as-received material recovered at 1.80 specific gravity. However, as with the bituminous coal, the weight recovery is quite low. For this char, crushing appears to be of no benefit, as the yield/ash relationship for the crushed char is essentially the same as for the as-received material.

It is apparent from these washability data that the apparent particle density of the chars is higher than that observed for coal. In most of the tests, less than 20 wt% of the char would float in liquids of 1.80 specific gravity. For most raw coals, upwards of 70 wt% would float in such liquids, with only the concentrated mineral matter occurring in the sink product. Also, for coal, crushing to a finer size typically improves the yield/ash relationship. For the chars, crushing was either of no value or resulted in a poorer yield/ash relationship.

To explain these observations, phenomena occurring during the formation of the chars must be considered. Under the high-temperature gasification conditions, the pore structure of the coal may collapse or otherwise be destroyed; and as a result, a denser form of carbon would exist in the char. Also under these conditions, the volatile matter is driven off. Loss of this relatively light material would also cause an increase in the apparent particle density. Finally, encapsulation of the mineral matter by the organic phase would increase the apparent particle density and also result in a more homogeneous material that would be difficult to beneficiate by physical means. Encapsulation of the ash would also explain why these gasification chars were less responsive to grinding for release of mineral matter than typical coals, since there would be less segregation of the various materials. We have visually observed under the microscope such encapsulation of the ash in other chars produced by similar high-temperature processing.

II. CONDITIONING OF COAL PRIOR TO PHYSICAL BENEFICIATION

EXPERIMENTAL

A unit has been designed and constructed to process coal and coal-derived materials with supercritical fluids. Figure 1 contains a sectional view of the heart of this apparatus, the supercritical fluid extraction vessel. The vessel is constructed entirely of 316 stainless steel and can be operated at conditions up to 673 K at 27.6 MPa. In the work reported here, the reflux column, which consists of a packed bed and condenser section, was maintained at the same temperature as the extraction section. The use of a temperature difference across the column to exploit the properties of supercritical fluids to fractionate non-distillable coal-derived liquids has been reported elsewhere [4].

The coal used in this work was a channel sample of Illinois No. 6 coal from the River King Mine containing 8.31 percent moisture, 13.33 percent ash, and 4.68 percent sulfur. Supercritical methanol (T_c = 512.6 K; P_c = 8.097 MPa), cyclohexane (T_c = 553.4 K; P_c = 4.074 MPa), and toluene (T_c = 591.7 K; P_c = 4.115 MPa) were used in the treatment of this coal. The solvents were obtained in drum quantities at greater than 99 percent purity and used as received.

A 500-gram charge of the coal, crushed to minus-14 mesh, is first placed in the extraction section of the supercritical fluid extraction vessel. After the unit is stabilized at operating conditions under a nitrogen atmosphere, the supercritical fluid is introduced into the bottom of the vessel through the sparger, where it contacts the coal. The fluid phase containing extracted material continues up the column and exits at the top of the vessel. The extracted material leaving the column is separated from the supercritical fluid by partial depressurization. The fluid is then condensed for reuse. Before being recycled in the unit, the solvents are distilled on a rotary evaporator.

The Illinois No. 6 coal was processed with methanol, cyclohexane, and toluene at a T_r, or T/T_c, of 1.02, and at a P_r, or P/P_c, of 2.0. The runs were terminated when the rate of collection of extracted material was less than 1 gram in 30 minutes. This required from 5 to 9 hours of operation. The flow of solvent was maintained at 0.27 gram-moles/minute during most of this work. This rate was doubled in one of the toluene treatments. No appreciable change was observed in the yield of extract in this case. To provide sufficient material for characterization and physical beneficiation testing, two runs were made with each solvent, and the respective products were combined. The yields of treated coal on a moisture-free basis were 90, 89, and 75 weight percent for methanol, cyclohexane, and toluene, respectively. The overall material balance, defined as the total weight of recovered material divided by the weight of the coal initially charged, ranged from 95 to 102 percent for all the tests.

Specific gravity separations of the treated coals were performed using conventional static float-sink techniques to determine their beneficiation potential.

DISCUSSION OF RESULTS

Tables 5 through 8 contain the results from the washability analysis of the Illinois No. 6 coal before and after treatment. These data are cumulative values and are reported on a moisture-free basis. Also shown in these tables are ash, total sulfur, and calorific value data obtained on the bulk samples prior to the specific gravity separations. The agreement between the bulk values and the results reconstituted from the washability data is generally acceptable. Noteworthy exceptions are the total sulfur contents of the coals treated with methanol and cyclohexane and the ash content of the toluene-treated coal. Additional work is being performed to find an explanation for these differences.

Reduction in total sulfur concentration is only observed in the specific gravity separation products of the methanol-treated coal. The higher total sulfur levels resulting from the cyclohexane and toluene treatments are primarily due to the extraction of a portion of the organic phase, which concentrates the remaining sulfur in the treated coal. The extractable materials from all of the tests contain approximately 2.4 wt% sulfur and no mineral matter. Sulfur balances for the treated coals using the bulk sample sulfur data are between 95 and 99 percent.

Unusually low levels of pyritic sulfur are reported for the cyclohexane-treated coal. The total sulfur, however, did not decrease by a corresponding amount, indicating either that organic sulfur was formed from the sulfur originally contained in the pyrite or that the analysis for pyritic sulfur is in error. Under the relatively mild reaction conditions, it is not likely that sulfur from the pyrite has incorporated into the organic matrix of the coal. Rather, the pyrite has probably been transformed into a form that does not dissolve in the acid used for the pyritic sulfur determination.

In contrast to the other treated coals, the total and pyritic sulfur levels in the toluene-treated coal remain high, even in the low specific gravity fractions. One possible explanation is that the toluene treatment caused a softening of the organic portion of the coal, resulting in increased encapsulation of the mineral matter. This would make the material more homogeneous with respect to the specific gravity separations. Softening of the coal was evidenced by the fact that the coal was mildly agglomerated after the toluene treatment. After treatment with either methanol or cyclohexane, however, the product was free-flowing and similar in appearance to the starting material.

Microscopic analysis of the various specific gravity fractions shows the toluene treatment produces particles that contain relatively more and larger pore openings than the particles after methanol or cyclohexane treatment. This characteristic could decrease the apparent specific gravities of the coal particles and result in the poor sulfur rejection observed for the toluene-treated coal. This phenomenon would explain the high yield in the Float-1.25 fraction. Several other coals have been treated to provide a larger frame of reference from which to investigate these observations.

In order to illustrate the changes in the true and/or apparent specific gravities of the coal particles resulting from the supercritical fluid treatments, the yield versus ash content data are plotted in Figure 2 for the raw and treated coals. In comparison with raw coal washability data, both the methanol and cyclohexane treatments marginally enhance the cleanability of the raw coal. In contrast, the toluene treatment makes it worse. Additional work with other solvents is in progress to determine if the positive trends observed with methanol and cyclohexane can be improved.

CONCLUSIONS

A set of three gasification chars have been subjected to physical beneficiation. In some cases, marginal improvements in the mineral matter content were achieved, but either unsatisfactory ash liberation or low yields were observed overall. The form of carbon in the ash is much denser than that typical for coal. One explanation for this observation is that some of the mineral matter has been encapsulated during the formation of the char. This is further evidenced by the poor response of the chars upon further size reduction. Other phenomena, such as loss of porosity and volatile matter, may also contribute to the poor separations observed. In summary, these observations highlight the inadequacy of conventional physical-cleaning methods for some coal-derived materials. If a clean char product is to be produced, either deeper initial cleaning of the coal is required or new techniques must be developed to separate the mineral matter from the resulting chars.

The washability of coal can be marginally improved through the use of an initial pretreatment with supercritical methanol or cyclohexane. Similar treatment with supercritical toluene has the opposite effect. While not presently practical from an economic standpoint, this work may provide new insights into possible avenues for producing alternative fuels from coal. More work needs to be done to determine if the mineral matter liberation can be further improved by varying the conditions and reagents used in the pretreatment.

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DISCLAIMER

Reference in this report to any specific product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

REFERENCES

1. McCown, F.E., Im, C.J., and Wolfe, R.A., Proceedings of the Second Annual Pittsburgh Coal Conference, 1985, 479.
2. Walters, A.B., ACS Fuel Division Preprints, 29(4), 1984, 337.
3. Kornosky, R.M., Gasior, S.J., Strakey, J.P., and Haynes, W.P, ACS Fuel Division Preprints, 22(2), 1977, 197.
4. Warzinski, R.P., ACS Fuel Division Preprints, 30(3), 1985, 139.

Table 1. Chemical Analysis of Gasification Chars

Coal Type	Subbituminous	Bituminous	Anthracite
Char Yield, wt% of Raw Coal	25	39	45
Proximate Analysis, wt%			
Moisture	1.8	1.3	0.5
Volatile Matter	5.8	1.7	3.1
Fixed Carbon	57.7	72.9	75.6
Ash	34.7	24.2	20.8
Ultimate Analysis, wt% mf			
Carbon	60.3	72.2	74.7
Hydrogen	1.2	1.4	1.1
Nitrogen	0.4	0.7	0.6
Oxygen	3.3	1.4	2.5
Sulfur	0.2	0.3	0.3
Ash	34.7	24.2	20.8
Calorific Value, Btu/lb	9,308	10,622	----

Table 2. Cumulative Washability Results for the Anthracite Coal Gasification Char

Products	--- As-Received ---				--- Crushed ---			
	Yield	Ash	Total Sulfur	Btu/lb	Yield	Ash	Total Sulfur	Btu/lb
	--- wt% mf ---				--- wt% mf ---			
Float 1.60	16.4	3.4	0.45	14,019	3.8	2.2	0.54	14,199
1.60 x 1.80	52.9	6.4	0.41	13,145	4.5	3.4	0.51	13,976
1.80 x 2.00	79.1	7.6	0.33	12,746	44.0	15.9	0.33	11,580
Sink 2.00	100.0	16.7	0.29	11,447	100.0	17.8	0.32	11,259

Table 3. Cumulative Washability Results for the Bituminous Coal Gasification Char

Products	--- As-Received ---				--- Crushed ---			
	Yield	Ash	Total Sulfur	Btu/lb	Yield	Ash	Total Sulfur	Btu/lb
	--- wt% mf ---				--- wt% mf ---			
Float 1.40	63.0	11.2	0.57	12,368	--0--	---	----	-----
1.40 x 1.60	77.2	11.5	0.53	12,265	19.5	3.8	0.80	13,100
1.60 x 1.80	87.0	12.8	0.49	12,103	20.5	4.1	0.78	13,041
1.80 x 1.90	100.0	17.8	0.45	11,354	23.0	5.1	0.73	12,894
1.90 x 2.00	----	----	----	-----	98.5	15.7	0.35	10,991
Sink 2.00	----	----	----	-----	100.0	17.0	0.35	10,953

Table 4. Cumulative Washability Results for the Subbituminous Coal Gasification Char

Products	As-Received Yield	As-Received Ash	As-Received Total Sulfur	As-Received Btu/lb	Crushed Yield	Crushed Ash	Crushed Total Sulfur	Crushed Btu/lb
	--- wt% mf ---				--- wt% mf ---			
Float 1.60	6.2	7.6	0.38	12,289	5.2	7.2	0.46	12,138
1.60 x 1.80	14.6	8.9	0.23	12,297	5.6	8.8	0.46	11,909
1.80 x 2.20	100.0	32.1	0.19	9,456	97.7	30.0	0.26	8,873
Sink 2.20	----	----	----	-----	100.0	30.1	0.28	8,860

Table 5. Cumulative Washability Results for Illinois No. 6 Coal

Products	Yield	Ash	Total Sulfur	Pyritic Sulfur	Btu/lb
	--- wt% mf ---				
Float 1.25	-0-	----	----	----	-----
1.25 x 1.28	3.4	3.1	2.60	0.45	13,777
1.28 x 1.30	12.8	2.6	2.67	0.37	13,836
1.30 x 1.40	67.5	5.4	3.12	0.78	13,492
1.40 x 1.60	86.4	7.6	3.40	1.14	13,450
Sink 1.60	100.0	13.8	5.02	2.92	12,410
Bulk Sample	-----	14.5	5.10	----	11,713

Table 6. Cumulative Washability Results for Methanol-Treated Illinois No. 6 Coal

Products	Yield	Ash	Total Sulfur	Pyritic Sulfur	Btu/lb
	--- wt% mf ---				
Float 1.25	-0-	----	----	----	-----
1.25 x 1.28	8.5	1.9	2.50	0.25	13,781
1.28 x 1.30	30.9	2.4	2.59	0.29	13,653
1.30 x 1.40	69.3	5.3	2.86	0.68	13,202
1.40 x 1.60	82.7	7.2	3.14	0.96	12,877
Sink 1.60	100.0	15.3	4.74	2.84	11,485
Bulk Sample	-----	14.9	5.29	----	11,601

Table 7. Cumulative Washability Results for Cyclohexane-Treated Illinois No. 6 Coal

Products	Yield	Ash	Total Sulfur	Pyritic Sulfur	Btu/lb
	--- wt% mf ---				
Float 1.25	7.4	2.3	2.88	0.41	13,847
1.25 x 1.28	25.5	3.4	2.90	0.19	13,826
1.28 x 1.30	42.7	3.1	3.02	0.16	13,713
1.30 x 1.40	72.7	5.5	3.42	0.17	13,339
1.40 x 1.60	86.4	7.5	3.85	0.18	13,036
Sink 1.60	100.0	14.7	4.38	1.03	12,031
Bulk Sample	-----	15.4	5.38	----	11,808

Table 8. Cumulative Washability Results for Toluene-Treated Illinois No. 6 Coal

Products	Yield	Ash	Total Sulfur	Pyritic Sulfur	Btu/lb
	--- wt% mf ---				
Float 1.25	42.4	8.3	3.22	1.44	12,885
1.25 x 1.28	50.0	8.5	3.24	1.48	12,869
1.28 x 1.30	53.6	8.3	3.21	1.46	12,938
1.30 x 1.40	73.0	8.6	3.22	1.50	12,863
1.40 x 1.60	83.5	9.8	3.41	1.70	12,672
Sink 1.60	100.0	17.3	5.51	3.92	11,465
Bulk Sample	-----	19.3	5.75	----	11,263

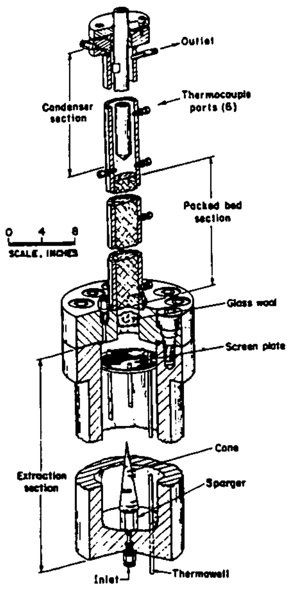

Figure 1. Sectional View of the Supercritical Fluid Extraction Vessel.

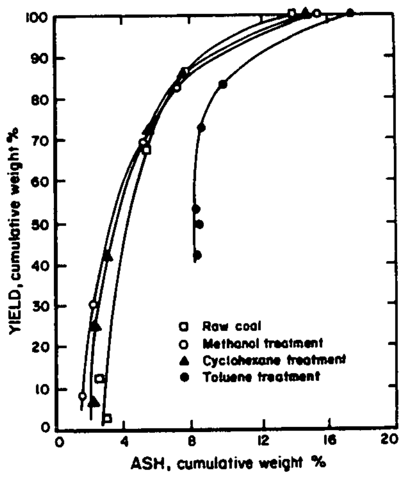

Figure 2. Comparison of Washability Data for Illinois No. 6 Coal Before and After Treatments with Supercritical Methanol, Cyclohexane, and Toluene.

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